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 - Japanese Laid-Open Patent Application 3-203159 (JP, A) ASAHI
 - Japanese Laid-Open Patent Application 52-70988 (JP, A) ASAHI
 - Japanese Laid-Open Patent Application 61-264663 (JP, A) MATSUSHITA

(54) [Title of the Invention] Explosion-Proof Secondary Cell

[Claims]

[Claim 1] An explosion-proof secondary cell basically comprising a positive electrode, a negative electrode, and a separator composed of a synthetic resin film having pores and including at least one member of the group consisting of low density

polyethylene (LDPE), linear low density polyethylene (LLDPE), and high density polyethylene (HDPE); wherein said cell is characterized by the fact that the internal impedance transition temperature ($t_1^{\circ}\text{C}$) is within the temperature range of at least 95°C and no higher than 160°C , and the internal impedance maximum temperature ($t_2^{\circ}\text{C}$) is at least not within the temperature range of $(t_1 + 10)^{\circ}\text{C}$, or, even if the above-mentioned internal impedance maximum temperature is within the temperature range of $(t_1 + 10)^{\circ}\text{C}$, then the ratio between the above-mentioned internal impedance at $(t_2 + 5)^{\circ}\text{C}$ and the above-mentioned internal impedance at $t_2^{\circ}\text{C}$ is at least 0.25 and less than 1.0.

[Claim 2] An explosion-proof secondary cell as defined in Claim 1, characterized by the fact that the film that forms the above-mentioned separator has a film resistance transition temperature ($t_3^{\circ}\text{C}$) within the temperature range of at least 95°C and no higher than 160°C , and the film resistance maximum temperature ($t_4^{\circ}\text{C}$) is at least not within the temperature range of $(t_3 + 10)^{\circ}\text{C}$, or, even if the above-mentioned film resistance maximum temperature is within the temperature range of $(t_3 + 10)^{\circ}\text{C}$, then the ratio between the above-mentioned film resistance at $(t_4 + 5)^{\circ}\text{C}$ and the above-mentioned film resistance at $t_4^{\circ}\text{C}$ is at least 0.25 and less than 1.0.

[Detailed Description of the Invention]

Field of Industrial Utilization

The present invention relates to a secondary cell, and more particularly relates to a secondary cell with superior safety at high temperatures.

Prior Art

Capacity and output have been steadily rising in recent years in primary cells, secondary cells, capacitors, condensers [sic], and other such electrical energy storage devices. Particularly in the case of cells, this has been accompanied by greater scrutiny of the issue of safety during short circuiting and other such malfunctions.

For instance, to take as an example lithium cells, the use of which has grown immensely in recent years, the cell temperature rises sharply when a short occurs inside or outside the cell, and this causes the cell contents to spurt out, and can even lead to an explosion.

To solve this problem, various attempts have been made at modifying the separator which separates the positive and negative electrodes. For example, in

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Japanese Laid-Open Patent Application 60-23954, it is proposed that a synthetic resin film having pores be used as the separator. Compared to a conventional separator made of a nonwoven cloth, this method is indeed fairly effective when an external short occurs in a single cell, but when it comes to shorts under harsher conditions, such as internal shorts, or external shorts in two or more single cells connected in series, the use of a synthetic resin film having pores as the separator is not effective.

Also, in Japanese Laid-Open Patent Application 1-186751 it is stated that, as a further improvement, the above-mentioned synthetic resin film having pores is coated with a low-melting point wax. This is undesirable because internal resistance increases at low temperatures, that is, within the range of actual usage temperatures, and is also undesirable because basic performance suffers even at close to room temperature since [the separator] is covered with a waxy insulating film.

*multi-layer
separator
distinguished*

Meanwhile, in Japanese Laid-Open Patent Application 63-308866 ^{Sample} is proposed the use of a laminate of two types of porous film, namely, polyethylene and polypropylene. Although an increase in the level of safety can be achieved in this case, there are problems in that, since two separators are used, the assembly process becomes more complicated, the cell volume increases, and the cost is higher.

Japanese Laid-Open Patent Applications 60-52, 61-232560, 62-283553, and 1-258358 relate to attempts at somehow improving on a separator made from a nonwoven cloth. However, when a nonwoven cloth with a large pore diameter is used as the substrate, the separator ends up being thicker, which is contrary to the goal of making the cell more compact and lightweight. Also, the temperature elevation that occurs during shorts is not sufficiently suppressed, and there is no effect against shorts under harsh conditions.

Problems Which the Invention is Intended to Solve

Although some of the above-mentioned conventional improvement means are effective in their improvement, they were inadequate on the following points.

For example, rupture, explosion, and other such problems can be prevented by the above-mentioned conventional improvements in the case of an external short, but in the case of shorts under harsher conditions, such as

- (1) shorts in assembled cells in which numerous cells are connected in series or parallel,
- (2) internal shorts that result in red heat,
- (3) shorts at high temperatures,

(4) shorts that accompany instantaneous destruction such as collapse or nailing, ✓
(5) shorts when the separator has deteriorated,
(6) dendritic shorts, or
(7) shorts caused by internal contact with the positive or negative electrode tabs, splitting or explosion can still occur, which poses the problem that damage or harm can come to nearby machinery, structures, or humans.

Accidents caused by such factors have been on the rise particularly in recent years, and ensuring safe operation under harsher conditions has been an urgent social need for some time. To this end, there is a need for further improvement to separators.

An object of the present invention is to solve the above problems and provide a cell with which safe operation can be preserved even during a malfunction, which is accomplished through the use of a separator with excellent safety.

Means Used to Solve the Above-Mentioned Problems

As a result of in-depth examination of the phenomena that occur during a short circuit or other malfunction in an effort to achieve the stated object, the inventors discovered that vastly superior safety characteristics are exhibited when special conditions are satisfied by the change in the internal impedance of a cell when the temperature thereof is raised at a specific rate.

It was also found that there is a correlation between the special conditions satisfied by the change in the internal impedance, and the special conditions satisfied by the change in the film resistance of the separator.

Specifically, the cell of the present invention is an explosion-proof secondary cell basically comprising a positive electrode, a negative electrode, and a separator ✓ composed of a synthetic resin film having pores and including at least one member of the group consisting of low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and high density polyethylene (HDPE); wherein said cell is characterized by the fact that the internal impedance transition temperature (t_1 °C) is within the temperature range of at least 95°C and no higher than 160°C, and the internal impedance maximum temperature (t_2 °C) is at least not within the temperature range of $(t_1 + 10)$ °C, or, even if the above-mentioned internal impedance maximum temperature is within the temperature range of $(t_1 + 10)$ °C, then the ratio between the above-mentioned internal impedance at $(t_2 + 5)$ °C and the above-mentioned internal impedance at t_2 °C is at least 0.25 and less than 1.0.

Here, it is preferable if the film that forms the separator has a film resistance transition temperature ($t_3^{\circ}\text{C}$) within the temperature range of at least 95°C and no higher than 160°C , and the film resistance maximum temperature ($t_4^{\circ}\text{C}$) is at least not within the temperature range of $(t_3 + 10)^{\circ}\text{C}$, or, even if the above-mentioned film resistance maximum temperature is within the temperature range of $(t_3 + 10)^{\circ}\text{C}$, then the ratio between the above-mentioned film resistance at $(t_4 + 5)^{\circ}\text{C}$ and the above-mentioned film resistance at $t_4^{\circ}\text{C}$ is at least 0.25 and less than 1.0.

Effect of the Invention

1 It is a long-held concept that safety can be ensured by designing a separator such that when a large short-circuit current flows and the internal temperature of a cell rises in the event of a short or other malfunction, the separator will soften and melt, so that its pores are blocked, which reduces the ion permeability and reduces the short-circuit current, the effect of which being that the temperature does not go over a specified level. With conventional methods such as these, however, rupture or explosion can still occur in the event of a short or other malfunction if the conditions are harsh, such as those discussed above.

2 As a result of in-depth examination of this phenomenon, the inventors discovered that when a conventional separator is used, the softening and melting of the separator as mentioned above during the elevation of the internal temperature does indeed result in the blockage of the separator pores, but at the same time, the melting and flow of the separator results in a loss of its original function, namely, the electrical insulation of the positive and negative electrodes, which ends up causing an even more severe short.

3 This phenomenon is particularly pronounced when the rise of the internal temperature is not uniform and there is a temperature distribution, when the temperature rises locally, and so on. It has come to light that this phenomenon is a major factor in the loss of safety.

4 In the present invention, the temperature at which the internal impedance of the cell rises during cell temperature elevation is extremely important.

5 The "film resistance transition temperature ($t_3^{\circ}\text{C}$)" in the present invention expresses the temperature at which the blockage of the separator pores begins, and is a value unconditionally defined by measurement of the change in film resistance during temperature elevation by the method discussed below. The "internal impedance transition temperature" is a value unconditionally defined by measurement of the

internal impedance of the cell by the same measurement method as for the film resistance transition temperature.

- 6 The film resistance transition temperature will be described below, but the description of the internal impedance transition temperature will be omitted since the method for measuring it is the same as that for the film resistance transition temperature, the only difference being the object of measurement.

- 7 [The film resistance transition temperature] is defined as the temperature at which the film resistance when the temperature has risen from 25°C first reaches 10 times the film resistance at 25°C. Specifically, this is the temperature at which the film resistance transition rate defined by the following formula first reaches 10.

$$\text{Film resistance transition rate} = R_t/R_{25}$$

R_t : film resistance at an arbitrary temperature of $t^\circ\text{C}$

R_{25} : film resistance at 25°C.

- 8 With the present invention, the internal impedance [transition temperature] ($t_1^\circ\text{C}$) and the film resistance transition temperature ($t_3^\circ\text{C}$) are at least 95°C and no higher than 160°C, and preferably at least 110°C and no higher than 155°C.

- 9 From the standpoint of ensuring safety, it is preferable for the internal impedance and film resistance transition temperatures to be lower than 95°C, but this is undesirable because the film resistance of the separator will rise within the temperature range in which a cell is normally used, so cell performance will suffer.

- 10 Also, it is undesirable for the internal impedance and film resistance transition temperatures to exceed 160°C because, as mentioned above, safe operation cannot be ensured when the internal cell temperature rises up this high.

- 11 As discussed above, to ensure safe operation against malfunction under all conditions, it is essential that the internal impedance transition temperature ($t_1^\circ\text{C}$) and film resistance transition temperature ($t_3^\circ\text{C}$) be within the temperature range of the above-mentioned conditions, but it is also important that the film resistance be high within the temperature range over these internal impedance and film resistance transition temperatures.

Specifically, the internal impedance maximum temperature $t_2^\circ\text{C}$ and the film resistance maximum temperature $t_4^\circ\text{C}$ are not within the temperature range from $t_1^\circ\text{C}$ to $(t_1 + 10)^\circ\text{C}$ and from $t_3^\circ\text{C}$ to $(t_3 + 10)^\circ\text{C}$, that is, the resistance value increases steadily within this temperature range, or, even if there is a resistance maximum value ($t_2^\circ\text{C}$ and $t_4^\circ\text{C}$) within the temperature range from $t_1^\circ\text{C}$ to $(t_1 + 10)^\circ\text{C}$ and from $t_3^\circ\text{C}$ to $(t_3 + 10)^\circ\text{C}$, the resistance ratios $(R_{t_2} + 5/R_{t_2})$ and $(R_{t_4} + 5/R_{t_4})$ from $t_2^\circ\text{C}$ to $(t_2$

+ 5)°C and from t_4 °C to $(Rt_4 + 5)$ °C are at least 0.25 and less than 1.0, and preferably at least 0.40 and less than 1.0, and more preferably at least 0.50 and less than 1.0. It is undesirable for $(Rt_2 + 5/Rt_2)$ and $(Rt_4 + 5/Rt_4)$ to be less than 0.25 because safe operation cannot be ensured. Furthermore, the film resistance maximum temperature t_4 °C is not within the temperature range from t_3 °C to $(t_3 + 10)$ °C, that is, the resistance value increases steadily within this temperature range, or, even if there is a resistance maximum value (t_4 °C) within the temperature range from t_3 °C to $(t_3 + 10)$ °C, the resistance ratio $(Rt_4 + 5/Rt_4)$ at t_4 °C and $(Rt_4 + 5)$ °C is at least 0.25 and less than 1.0, and preferably at least 0.40 and less than 1.0, and more preferably at least 0.50 and less than 1.0. It is undesirable for $(Rt_4 + 5/Rt_4)$ to be less than 0.25 because safe operation cannot be ensured.

An antinomic relationship exists in a separator trying to satisfy both of these conditions simultaneously, and achieving this goal is fraught with problems.

Specifically, it is an extremely important requirement in terms of ensuring safety that the ion permeability and the short-circuit current be reduced by the softening and melting of the separator and the blockage of the pores thereof when a large short-circuit current flows through the cell and causes the internal cell temperature to rise.

This phenomenon occurs in the vicinity of the "film resistance transition temperature (t_3 °C)" referred to in the present invention. If the separator further melts and softens, this is actually a negative because the separator will lose its original function of electrically insulating the positive and negative electrodes, and the internal short circuit will conversely be increased at the same time.

This phenomenon is exposed as a particularly grave problem when the rise of the internal temperature is not uniform and there is a temperature distribution, when the temperature rises locally, and so on, which frequently happens during the malfunction of an actual cell, and this leads to problems such as rupture and explosion. With a conventional separator, it was impossible to satisfy both of these antinomic requirements at the same time.

As a result of various studies, the inventors discovered the following several methods for obtaining a cell that satisfies the requirements of the present invention, although this list is not intended to be comprehensive.

(1) Methods that make use of a special separator.

(2) Methods in which a substance (such as a three-dimensionalized methacrylic or acrylic resin) having the property of absorbing electrolytic solution above a certain temperature is made to be present inside the cell, inside the positive and negative electrodes, inside the separator, and so on.

(3) Methods in which a substance exhibiting a thickening action on electrolytic solution above a certain temperature is made to be present inside the cell, inside the positive and negative electrodes, inside the separator, and so on.

(4) Methods in which microencapsulated mineral oil, wax, or another such insulating substance is made to be present inside the cell, inside the positive and negative electrodes, and inside the separator.

With (1), there are no particular limitations, but [the goal] is achieved through selection and combination of the separator material, the molecular weight or molecular weight distribution, the shape of the pores in the separator, the separator thickness, the surface structure of the separator, the surface condition, the degree of elongation of the separator, aleotropy, and various other such factors.

Let us give an example of this, although other cases are also possible. A particularly important element in the selection of the separator material is that the film resistance transition temperature ($t_3^{\circ}\text{C}$) be confined to within the range of the present invention. As one material selection criterion, it is possible to select a material whose glass transition temperature (T_g), melting point (T_m), and the like are within a temperature range of 95 to 160°C. Examples of such materials include low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and high density polyethylene (HDPE), one or more of which may be used.

Molecular weight, molecular weight distribution, the shape of the pores in the separator, the degree of elongation of the separator, aleotropy, and the like are important in terms of maintaining the film resistance value in a temperature region over the film resistance transition temperature ($t_3^{\circ}\text{C}$). To give a criterion for selecting these, a higher molecular weight is preferable. However, a higher molecular weight means that moldability is sacrificed, so some modification must, of course, be made to the molding method or the pore formation method. For instance, a plasticizer must be used or, in some cases, the molecular weight distribution must be expanded by mixture of materials with high and low molecular weights, for example.

As to the shape of the pores in the separator, a shape in which the pores are formed in a straight line with respect to the thickness direction (such as when pores are obtained by a method featuring drawing, which is known as a method for manufacturing Celgard (trade name of a product of the U.S. firm of Celanese)) is undesirable. A reticulated pore shape obtained by extraction or another such manufacturing method is favorable. As to drawing, a separator that has undergone excessive drawing is undesirable because of the high degree of heat shrinkage.

Although not a particular requirement in the present invention, it is preferable for the film resistance at 25°C (R25), which is a basic aspect of performance, to be lower, and R25 is usually 0.5 to 50 $\Omega\cdot\text{cm}^2$, preferably 5 to 20 $\Omega\cdot\text{cm}^2$, and even more preferably 0.5 to 10 $\Omega\cdot\text{cm}^2$.

Again, while not a particular requirement, the air permeability is no more than 300 sec/100 cc, and preferably 200 sec/100 cc, and even more preferably 150 sec/100 cc.

There are no particular restrictions on the thickness of the separator, but it is usually 5 to 500 μ , with a range of 10 to 100 μ being preferable, and 10 to 50 μ being even better. Less than 5 μ is undesirable because the separator will be so thin that it loses its insulating function, but exceeding 500 μ is also undesirable because the volume will be greater, which is contrary to the goal of obtaining a cell that is compact and lightweight.

There are no particular restrictions on the diameter of the separator pores, either, but the average pore diameter is usually 0.01 to 10 μ , with 0.05 to 5 μ being preferable and 0.05 to 0.5 μ being even better.

There are no particular restrictions on the air permeability, but 35 to 85% is favorable, and 50 to 80% is preferable.

There are no particular restrictions on the "cell" referred to in the present invention, but examples thereof include lithium cells, manganese-zinc cells, silver-zinc cells, and other such primary cells, and nickel-cadmium cells, nickel-zinc cells, nickel-hydrogen cells, polymer cells, lithium secondary cells, carbon secondary cells, and other such secondary cells.

As a result of using a separator that satisfies all the requirements of the present invention, there is a marked increase in cell safety, and there is no rupture, explosion, or other such phenomena in the event of a short circuit, reverse charging, overcharging, or other such malfunction under harsh conditions.

Practical Examples

Practical examples will now be given in order to describe the present invention in more detail, but the present invention is not limited to or by these practical examples.

The various properties discussed were measured by the following methods.

Internal impedance transition temperature ($t_1^{\circ}\text{C}$) and internal impedance maximum temperature ($t_2^{\circ}\text{C}$)

A thermocouple is attached to the cell case wall, and while the impedance is continuously measured at a frequency of 1 kHz, the cell is heated from 25°C to 175°C in an oven set at a temperature elevation rate of $2^{\circ}\text{C}/\text{min}$. The temperature at which a value ten times greater than the impedance at 25°C is first reached is measured, and this temperature is termed the internal impedance transition temperature ($t_1^{\circ}\text{C}$). The temperature is further raised, and if there is a maximum value to the impedance within the temperature range from $t_1^{\circ}\text{C}$ to $(t_1 + 10)^{\circ}\text{C}$, then this temperature is measured and termed the internal impedance maximum temperature ($t_2^{\circ}\text{C}$).

Film resistance

Figure 1 shows the apparatus used to measure the film resistance defined in the present invention. In Figure 1 (A), 1A and 1B are nickel foils with a thickness of $10\ \mu$, and are connected to an impedance measurement apparatus 8. As shown in Figure 1 (C), the nickel foil 1A has been masked with a Teflon tape 6 such that a rectangle measuring 15 mm high and 10 mm wide is left exposed. 3 is a separator impregnated with a specific electrolytic solution, and is positioned between 1A and 1B, with its four sides fixed by Teflon tape. 5 is a thermocouple that is used to measure the temperature, and is attached with Teflon tape to a glass plate 2B. The space between glass plates 2A and 2B is filled with a specific electrolytic solution.

The nickel foils 1A and 1B, the glass plates 2A and 2B, the separator 3, and the thermocouple 5 are all housed in a case 4 as shown in Figure 1B. 9 is a recording apparatus used to record the temperature and the measured impedance.

A 1 M lithium borofluoride/propylene carbonate solution is used as the electrolytic solution. Measurement is conducted at 25°C , the measurement frequency is 1 kHz, and the film resistance R_{25} at 25°C is determined from the following equation.

$$R_{25} = \text{measured value } (\Omega) \times 1\text{ cm} \times 1.5\text{ cm (units: } \Omega \cdot \text{cm}^2)$$

Film resistance transition temperature ($t_3^{\circ}\text{C}$) and film resistance maximum temperature ($t_4^{\circ}\text{C}$)

While the impedance is continuously measured using the film resistance measurement apparatus shown in Figure 1, the cell is heated from 25°C to 175°C in an oven set at a temperature elevation rate of $2^{\circ}\text{C}/\text{min}$. The temperature at which a value ten times greater than the impedance at 25°C is first reached is measured, and this

temperature is termed the film resistance transition temperature ($t_3^{\circ}\text{C}$). The temperature is further raised, and if there is a maximum value to the impedance within the temperature range from $t_3^{\circ}\text{C}$ to $(t_3 + 10)^{\circ}\text{C}$, then this temperature is measured and termed the film resistance maximum temperature ($t_4^{\circ}\text{C}$).

Molecular weight

The weight average molecular weight (\bar{M}_w) and number average molecular weight (\bar{M}_n) are measured under the following conditions.

GPC measurement apparatus: Model 200 made by Waters

Column: 7000S to G and 3000S made by Tosoh

Solvent: trichlorobenzene

Measurement temperature: 135°C

Porosity

Porosity is calculated from the following equation.

$$\text{Porosity} = \frac{\text{pore volume}}{\text{porous film volume}} \times 100 (\%)$$

Pore volume = weight of contained water - bone dry weight

Average pore diameter

This is calculated by taking a weighted average of the major and minor axes of 200 pores observed in a scanning electron micrograph of the porous film surface. The units are in microns.

Air permeability

This is measured according to Method A in ASTM D-726. The units are in seconds/100 cc·sheet.

Practical Example 1

This practical example is a separator manufacturing example.

13 vol% pulverized silicic acid and 61.5 vol% dioctyl butylphthalate were mixed in a Henschell mixer, to which 25.5 vol% high density polyethylene with a weight average molecular weight (\bar{M}_w) of 600,000 and a M_w/M_n of 15 was added, and the components were again mixed in the Henschell mixer.

✓ This mixture was kneaded and made into pellets in a twin-screw extruder with a diameter of 30 mm. These pellets were molded into a film with a thickness of $100\ \mu$ in a film manufacturing apparatus comprising a T-die with a width of 450 mm attached to a twin-screw extruder with a diameter of 30 mm. The molded film was soaked for 5 minutes in 1,1,1-trichloroethane to extract the DOP, after which it was dried and then soaked for 30 minutes in 70°C 20% caustic soda to extract the pulverized silicic acid, after which this product was dried, which yielded a porous film.

This porous film was then drawn to a factor of 2.7 in the longitudinal direction by a roll drawing machine heated to 115°C , and then subjected to a heat treatment for 10 seconds in a 120°C atmosphere. The properties of the film obtained from the above procedure are given in Table 1. The change in the film resistance during temperature elevation is indicated by the curve A in Figure 2. Table 2 shows the film resistance transition temperature ($t_3^{\circ}\text{C}$) and the film resistance maximum temperature ($t_4^{\circ}\text{C}$).

Practical Example 2

This practical example is a separator manufacturing example.

extract Other than the use of a high density polyethylene with a weight average molecular weight of 850,000 and a Mw/Mn of 15, the same operation as in Practical Example 1 was carried out. The properties of the film thus obtained are given in Table 1. The change in the film resistance during temperature elevation is indicated by the curve B in Figure 2.

A comparative example will now be given in order to check the characteristics of the films obtained in Practical Examples 1 and 2.

Comparative Example 1

This comparative example is a separator manufacturing example.

80% [Other than the use of a high density polyethylene with a weight average molecular weight of 80,000 and a Mw/Mn of 13, the same operation as in Practical Example 1 was carried out. The properties of the film thus obtained are given in Table 1. The change in the film resistance during temperature elevation is indicated by the curve ~~C~~ ^D in Figure 2. Table 2 shows the film resistance transition temperature ($t_3^{\circ}\text{C}$) and the film resistance maximum temperature ($t_4^{\circ}\text{C}$). ✓

Practical Example 3

This practical example is a separator manufacturing example.

Other than the use of a high density polyethylene with a weight average molecular weight of 430,000 and a Mw/Mn of 13, the same operation as in Practical Example 1 was carried out. The properties of the film thus obtained are given in Table 1. The change in the film resistance during temperature elevation is indicated by the curve C in Figure 2.

Table 1

	Film thickness (μ)	Porosity (%)	Average pore diameter (μ)	Air permeability (sec/100 cc·sheet)	Film resistance (Ω ·cm ²)
P. E. 1	28	62	0.07	100 (25°C)	3.1
P. E. 2	30	51	0.11	135 (25°C)	4.3
C. E. 1	33	55	0.09	151 (25°C)	8.3
P. E. 3	38	51	0.03	108 (25°C)	9.2

P. E.: Practical Example, C. E.: Comparative Example

Practical Example 4

The "C" cell shown in Figure 3 was manufactured using manganese dioxide as the positive electrode active material, using graphite and acetylene black as conductive agents, using tetrafluoroethylene as a binder, using as the positive electrode a sheet obtained by coating a stainless steel lath with an aqueous paste comprising a mixture of manganese dioxide, graphite, acetylene black, and tetrafluoroethylene (in a weight ratio of 85:5:5:5, respectively) and then drying this coating, and using a lithium metal foil as the negative electrode. Figure 3 is a half cross section of a coiled cell. Here, 11 is the positive electrode, 12 is the separator, 13 is the negative electrode, 14 is an insulation plate, 15 is a negative electrode lead, 16 is a positive electrode lead, and 17 is a gasket.

The film obtained in Practical Example 1 was used as the separator 3,* and a liquid obtained by dissolving lithium perchlorate in a concentration of 1.0 M in a mixed solvent (volume ratio: 1:1) of propylene carbon and dimethoxyethane was used as the

* Translator's note: Labelled "12" above and in the figure.

Comparative Example 2

Other than the use of the film obtained in Comparative Example 1 as the separator, the same operation as in Practical Example 4 was carried out. The t_1 of this cell was 133°C, and the t_2 was 140°C. The ratio of the impedance at 145°C and at 140°C was 0.15. Table 3 shows the various test evaluation results for this cell.

Comparative Examples 3 to 5

Other than the use of the separators shown in Table 2 as the separator, the same operation as in Practical Example 4 was carried out. Table 3 shows the various test evaluation results for these cells. The t_1 of these cells was 169°C, 137°C, and > 175°C, respectively. The t_2 of the cell in Comparative Example 4 was 139°C, and the ratio of the impedance at 144°C and at 139°C was 0.05. Figure 4 shows curves of the film resistance change when the temperature was elevated for the separators used here. Curves E, F, and G indicate the film resistance change for Comparative Examples 3, 4, and 5, respectively. Table 2 shows the film resistance transition temperature (t_3 °C) and the film resistance maximum temperature (t_4 °C).

Practical Example 7

Other than the use of the film obtained in Practical Example 2 as the separator, the same operation as in Practical Example 5 was carried out. The t_1 of this cell was 137°C, and the t_2 was 144°C. The ratio of the impedance at 149°C and at 144°C was 0.83. Table 3 shows the various test evaluation results for this cell.

Practical Example 8

Other than the use of the film obtained in Practical Example 3 as the separator, the same operation as in Practical Example 5 was carried out. The t_1 of this cell was 116°C, and the t_2 was 121°C. The ratio of the impedance at 126°C and at 121°C was 0.30. Table 3 shows the various test evaluation results for this cell.

Comparative Examples 6 to 8

Other than the use of the separators shown in Table 2 as the separator, the same operation as in Practical Example 5 was carried out. Table 3 shows the various test evaluation results for these cells. The t_1 of these cells was 169°C, 137°C, and >175°C, respectively. The t_2 of the cell in Comparative Example 7 was 139°C, and the ratio of the impedance at 144°C and at 139°C was 0.05. Figure 4 shows curves of the film resistance change when the temperature was elevated for the separators used here. Curves E, F, and G indicate the film resistance change for Comparative Examples 6, 7, and 8, respectively. Table 2 shows the film resistance transition temperature (t_3 °C) and the film resistance maximum temperature (t_4 °C).

Table 2

Separator	Film resistance transition temp. (t_3 °C)	Film resistance maximum temp. (t_4 °C)	Ratio of film resistance at t_4 °C and $t_4 + 5$ °C ($R_{t_4 + 5°C}/R_{t_4°C}$)
Prac. Ex. 1 A	135°C	no max.*1	—
Prac. Ex. 2 B	137°C	144°C	0.83
Comp. Ex. 1 D	133°C	140°C	0.15
Celgard 2500*2	169°C	170°C	0.03
Celgard K878*2	137°C	139°C	0.05
Nonwoven cloth*3	>175°C*4	none	—
Prac. Ex. 3 C	116°C	121°C	0.30

*1: No maximum temperature in the range of $t_3 + 10$ °C

*2: 25 μ polypropylene film made by Celanese

*3: Nonwoven cloth made of 100 μ polypropylene

*4: No transition temperature up to 175°C



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A
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Table 3 — Cell test evaluation results

	Separator used	External 0 Ω rating	External 0 Ω short* ¹ (2 cells in series)	Nailing rating* ² in series)	Overcharging test* ³ (1 cell)
P. E. 4	P. E. 1	O (128°C)	O (131°C)	O (112°C)	O (115°C)
P. E. 5	P. E. 1	O (125°C)	O (130°C)	O (109°C)	O (118°C)
P. E. 6	P. E. 2	O (129°C)	O (132°C)	O (110°C)	O (125°C)
P. E. 7	P. E. 2	O (133°C)	O (135°C)	O (116°C)	O (121°C)
P. E. 8	P. E. 3	O (116°C)	O (119°C)	O (98°C)	leakage
C. E. 2	C. E. 1	O (133°C)	O (136°C)	rupture	rupture
C. E. 3	Celgard 2500	rupture	rupture	rupture	rupture
C. E. 4	Celgard K-878	O (136°C)	rupture	rupture	rupture
C. E. 5	nonwoven cloth	rupture	rupture	rupture	rupture
C. E. 6	Celgard 2500	rupture	rupture	rupture	rupture
C. E. 7	Celgard K-878	O (137°C)	rupture	rupture	rupture
C. E. 8	nonwoven cloth	rupture	rupture	rupture	rupture

*1: A short circuit was induced with two cells in series.

*2: A nail with a diameter of 3 mm is hammered into the cell case.

*3: Current was passed through for 10 hours at a 2 A constant current and 9 V maximum voltage.

The numbers in parentheses are the maximum attained temperature

Merits of the Invention

As described above, the merits of the cell pertaining to the present invention are that no rupture, explosion, or other such phenomena occur during a short circuit or other malfunction under harsh conditions, and performance with excellent safety and reliability can be achieved.

[Brief Description of the Figures]

Figure 1 shows the apparatus used to measure the film resistance defined in the present invention;

Figure 2 is a graph of the change in film resistance during separator temperature elevation in the practical examples of the present invention and comparative examples*;

Figure 3 is a half cross section of a coiled cell in the practical examples of the present invention and comparative examples; and

Figure 4 is a graph of the change in film resistance during separator temperature elevation in the comparative examples.

Key:

* Translator's note: Only practical example curves given.

1A and 1B ... nickel foils
2A and 2B ... glass plates
3 and 12 ... separators
4 ... case
5 ... thermocouple
6 ... Teflon tape
8 ... impedance measurement apparatus
9 ... recorder
11 ... positive electrode
13 ... negative electrode
14 ... insulation plate
15 ... negative electrode lead
16 ... positive electrode lead
17 ... gasket

Figure 1 — Diagram of the apparatus used to measure film resistance defined in present invention.

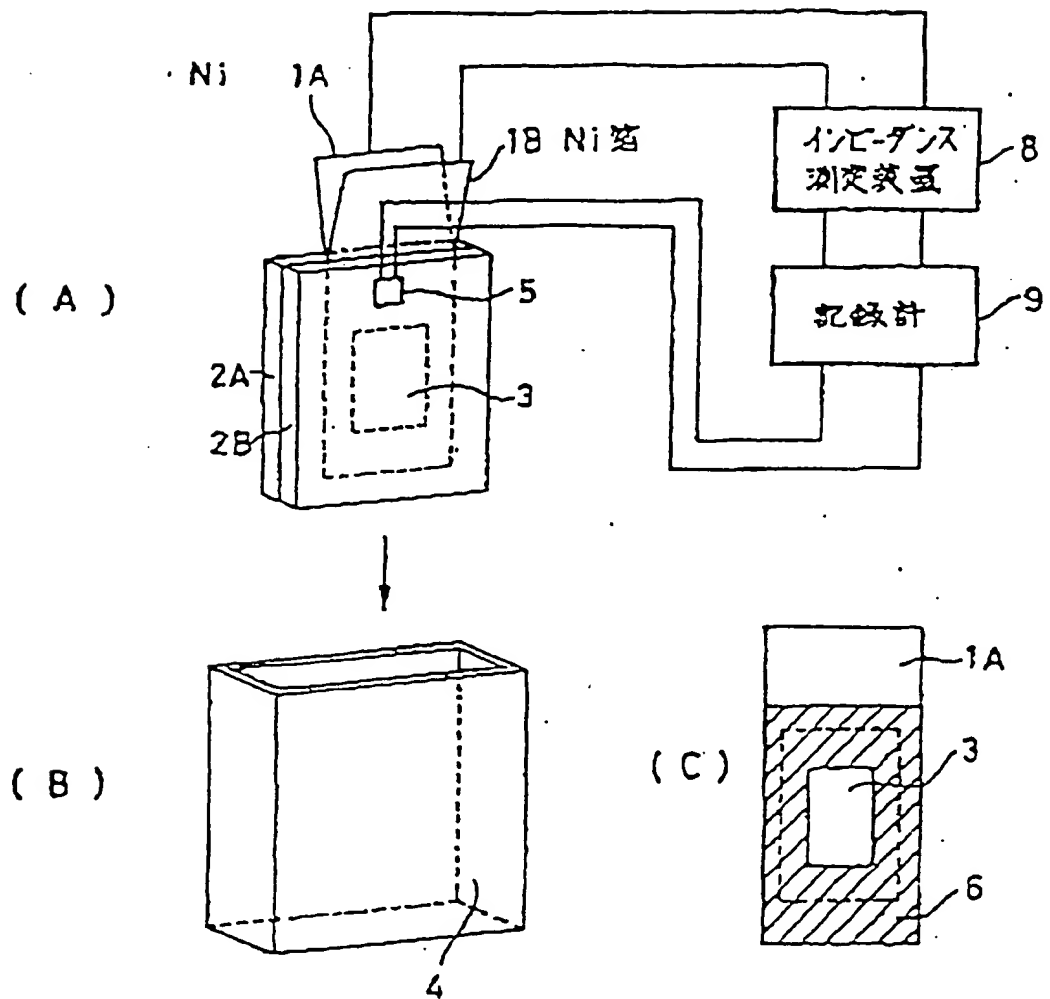


Figure 2 — Graph of change in film resistance during separator temperature elevation in practical examples of present invention

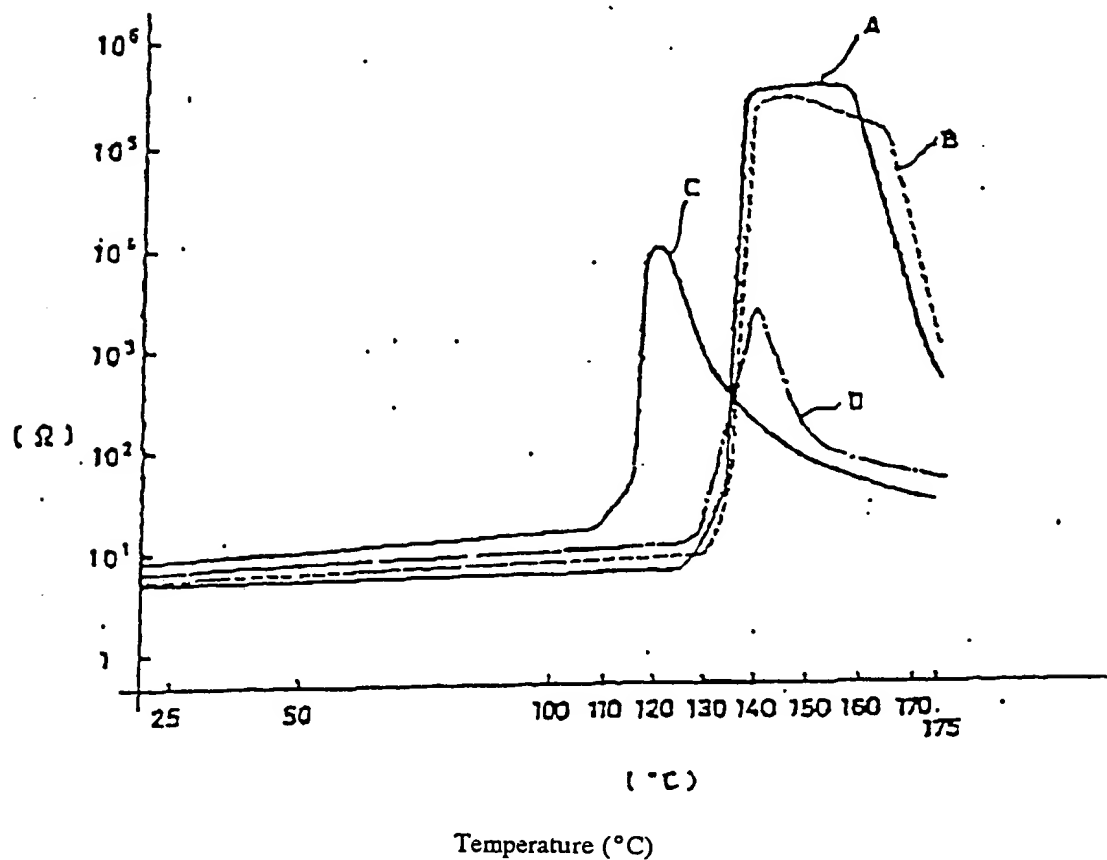


Figure 3 — Half cross section of coiled cell in practical examples of present invention and comparative examples

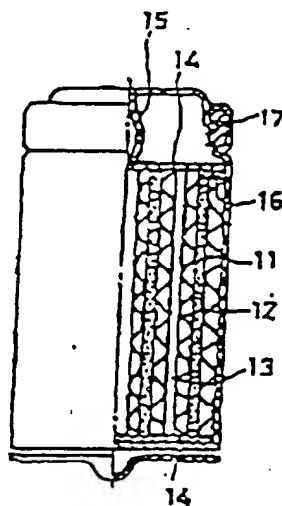
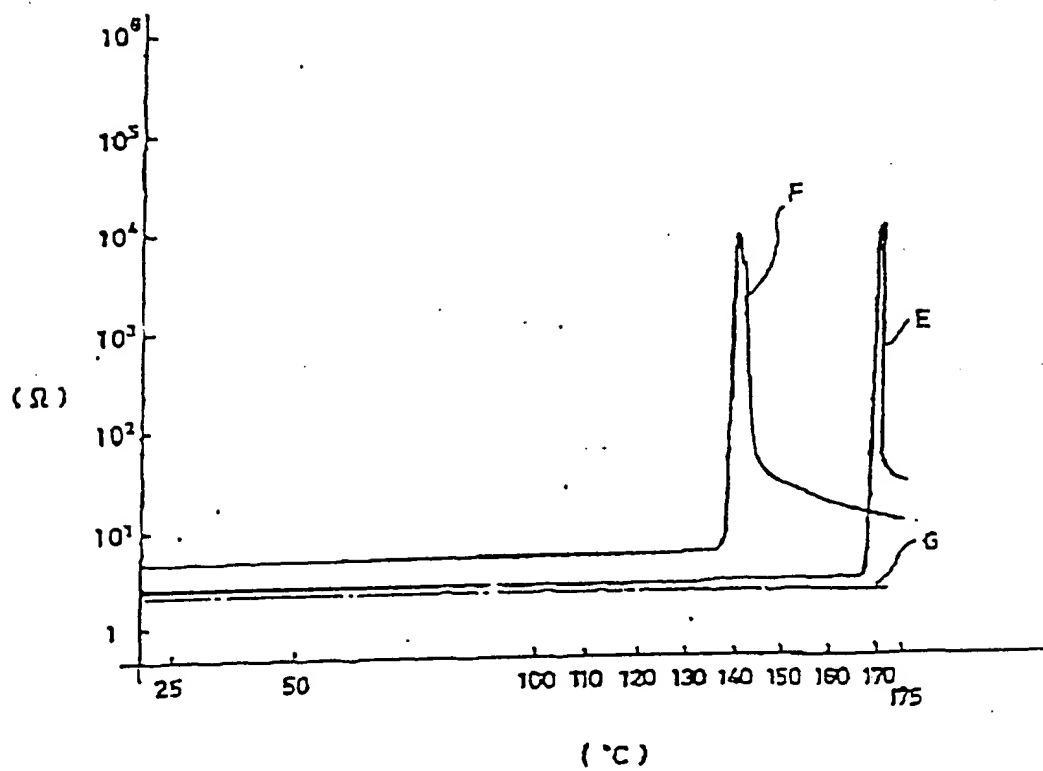


Figure 4 — Graph of change in film resistance during separator temperature elevation in comparative examples



Temperature (°C)

nickel foil 1A
1B nickel foil

impedance
measurement
apparatus

5 thermocouple
glass plate 2A
glass plate 2B
3 separator
recorder
3 separator
6 Teflon tape

Film resistance (Ω)

15 negative electrode lead
14 insulation plate
17 gasket
16 positive electrode lead
11 positive electrode
12 separator
13 negative electrode
14 insulation plate

Film resistance (Ω)

Amended Claim

[claim 1]

An explosion-proof secondary cell in the form of a coiled cell basically comprising a positive electrode which is obtained by coating an aluminum foil with a positive electrode active material, a positive electrode lead which is connected to the positive electrode, a negative electrode which is obtained by coating a copper foil with a negative electrode active material, a negative electrode lead which is connected to the negative electrode, and a separator which is composed of a single-ply, synthetic resin film having pores and containing at least one polymer selected from the three types of low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and high density polyethylene (HDPE); and said separator having a film resistance transition temperature (t_3 , °C) within the temperature range of at least 95 °C and no higher than 160°C, and said separator not having the film resistance maximum temperature (t_4 , °C) at least within the temperature range of (t_3+10) °C; or, even if said separator has the above-mentioned film resistance maximum temperature within the temperature range of (t_3+10) °C, then the ratio between the above-mentioned film resistance at (t_4+5) °C and the above-mentioned film resistance at t_4 , °C of is least 0.25 and less than 1.0; wherein the internal impedance transition temperature (t_1 , °C) is within the temperature range of at least 95°C and no higher than 160°C, and the internal impedance maximum temperature (t_2 , °C) is at least not within the temperature range of (t_1+10) °C, or, even if the above-mentioned internal impedance maximum temperature is within the temperature range of (t_1+10) °C, then the ratio between the above-mentioned internal impedance at (t_2+5) °C and the above-mentioned internal impedance at (t_2+5) °C and the above-mentioned internal impedance at t_2 , °C is at least 0.25 and less than 1.0.